

## REOXIDATION OF BIOREDUCED URANIUM UNDER REDUCING CONDITIONS

Jiamin Wan, Tetsu Tokunaga, Eoin Brodie, Zeming Wang<sup>1</sup>, Zuoping Zheng, Don Herman<sup>2</sup>,  
Terry Hazen, Mary Firestone<sup>2</sup>, and Stephen R. Sutton<sup>3</sup>

<sup>1</sup>Pacific Northwest National Laboratory; <sup>2</sup>University of California, Berkeley; <sup>3</sup>University of Chicago

Contact: Jiamin Wan, 510/486-6004 jmwan@lbl.gov

### RESEARCH OBJECTIVES

Interest in the biogeochemical cycle of uranium (U) is growing, especially for remediating contaminated environments. The mobility of U depends strongly on its oxidation state, with U(IV) being much less soluble than U(VI). Therefore, some strategies under development for immobilizing U in contaminated sediments are aimed at promoting precipitation of U(IV) minerals, typically by injecting organic carbon (OC) into sediments to stimulate microbial U(VI) reduction. Previously, observations of OC-stimulated U reduction have only reported fairly short-term results. Our studies are directed at understanding the conditions controlling longer-term stability of bioreduced U.

### APPROACH

Columns packed with a U contaminated (206 mg kg<sup>-1</sup>) sediment obtained from the Natural and Accelerated Bioremediation (NABIR) Program's Field Research Center in Oak Ridge National Laboratory were supplied with sodium lactate (32 mM OC) solutions, and effluent solution chemistry was monitored. U oxidation states were determined nondestructively in soil columns at the Advanced Photon Source, GSECARS beamline, by micro-X-ray absorption spectroscopy (micro-XAS). Fluorescence spectroscopic measurements were conducted to determine the U species in effluents. Microbial communities within sediment columns were characterized by high-density oligonucleotide array analyses and real-time quantitative polymerase chain reaction methods.

### ACCOMPLISHMENTS

Our 17-month study showed that bioreduction of U was transient, even under sustained reducing conditions. Micro-XAS showed that U was reduced during the first 80 days, but later (100 to 500 days) reoxidized and solubilized (Figure 1), although a microbial community capable of reducing U(VI) was maintained. OC-stimulated microbial respiration caused increases in (bi)carbonate concentrations and formation of uranyl carbonate complexes, thereby increasing the favorability of U(IV) oxidation. Fluorescence spectroscopy showed that U(VI) in effluents occurred primarily as uranyl tricarboxylate and dicalcium uranyl tricarboxylate. We hypothesize that kinetic

limitations allowed Fe(III) to persist as terminal electron acceptors for U reoxidation.

### SIGNIFICANCE OF FINDINGS

These results show that *in situ* U remediation by OC-based reductive precipitation can be problematic in sediments when uranyl carbonates are stable, and that OC concentrations in remedial solutions need to be carefully considered to minimize carbonate-enhancement of U(VI) solubility. This work also demonstrates the need for long-term experiments to evaluate remediation strategies that rely on transforming actinides and metals to low-solubility products. In considering much longer time scales set by the half-life of <sup>238</sup>U, the practicality of reduction-based immobilization strategies in regionally oxidizing sediments needs to be carefully reevaluated.

### RELATED PUBLICATIONS

Tokunaga, T.K., J. Wan, J. Pena, E. Brodie, M.K. Firestone, T.C. Hazen, S.R. Sutton, A. Lanzarotti, and M. Newville. Uranium reduction in sediments under diffusion-limited transport of organic carbon. *Environ. Sci. Technol.* (in final review), 2005.

Wan, J., T.K. Tokunaga, E. Brodie, Z. Wang, Z. Zheng, D. Herman, T.C. Hazen, M.K. Firestone, and S.R. Sutton. Reoxidation of bioreduced uranium under reducing conditions. *Environ. Sci. Technol.*, 39 (in press), 2005. Berkeley Lab Report LBNL-56058.

### ACKNOWLEDGMENTS

This project is supported by the Director, Office of Science, Office of Biological and Environmental Research, NABIR Program, and Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences, of the U.S. Department of Energy under Contract No. DE-AC03-76-SF00098. Use of the Advanced Photon Source was supported by the DOE, Basic Energy Sciences, Office of Science. Fluorescence spectroscopic measurements were performed at the Environmental Molecular Sciences Laboratory, sponsored by the Office of Biological and Environmental Research. We thank J. Larsen, D. Joyner, S. Baek, J. Pena, and M. Newville for technical assistance.

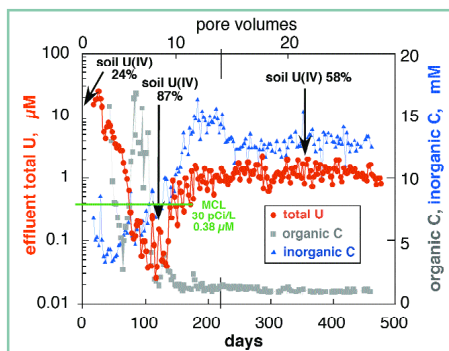


Figure 1. Concentrations of U, OC, and bicarbonate concentrations in effluents from columns supplied with 32 mM OC. Micro-XAS showed that the soil U was initially oxidizing (24% U(IV)), then largely reduced (87% U(IV)), and later reoxidized (58% U(IV)).